(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 137 598 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent: 23.04.2003 Bulletin 2003/17

(51) Int Cl.7: C01G 51/00, C01G 1/00, H01M 4/52

(21) Application number: 99960299.8

(22) Date of filing: 12.11.1999

(86) International application number: PCT/US99/26758

(87) International publication number: WO 00/029331 (25.05.2000 Gazette 2000/21)

Quenched LMO_2 better fade than slow-cooled

(54) LAYERED LITHIUM METAL OXIDES FREE OF LOCALIZED CUBIC SPINEL-LIKE STRUCTURAL PHASES AND METHODS OF MAKING SAME

SCHICHTGITTERSTRUKTUR BESITZENDE LITHIUMHALTIGE METALLOXIDE, DIE FREI VON LOKALEN KUBISCH-SPINELL-ARTIGEN PHASEN SIND, UND HERSTELLUNG DERSELBEN

OXYDES DE LITHIUM METALLIQUE STRATIFIE EXEMPT DE PHASES STRUCTURELLES SPINELLO DES CUBIQUES LOCALIS ES ET PROCEDE DE FABRICATION

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

(30) Priority: 13.11.1998 US 108360 P

(43) Date of publication of application: 04.10.2001 Bulletin 2001/40

(73) Proprietor: FMC CORPORATION
Philadelphia, PA 19103 (US)

(72) Inventors:
- GAO, Yuan
  Ocean, NJ 07712 (US)
- YAKOVLEVA, Marina
  Gastonia, NC 28054 (US)
- WANG, Hugh, H.
  Brandon, FL 33511 (US)
- ENGEL, John, F.
  Belmont, NC 28012 (US)

(74) Representative: Hucker, Charlotte Jane
Gill Jennings & Every
Broadgate House,
7 Eldon Street
London EC2M 7LH (GB)

(56) References cited:
EP-A- 0 646 546
EP-A- 0 672 622
WO-A-97/07555
CA-A- 2 123 489

- BOYLE T J ET AL: "RECHARGEABLE LITHIUM BATTERY CATHODES. NONAQUEOUS SYNTHESIS, CHARACTERIZATION, AND ELECTROCHEMICAL PROPERTIES OF LICOO2" CHEMISTRY OF MATERIALS,US,AMERICAN CHEMICAL SOCIETY, WASHINGTON, vol. 10, no. 8, 1 August 1998 (1998-08-01), pages 2270-2276, XP000776652 ISSN: 0897-4756
- PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) & JP 11 016573 A (SUMITOMO METAL MINING CO LTD), 22 January 1999 (1999-01-22) & CHEMICAL ABSTRACTS, vol. 130, no. 10, 1999 Columbus, Ohio, US; abstract no. 127482, A. YAMANAKA, R. KATSURAO, T. TSUJIMURA: "Lithium cobalt mixed oxides for cathodes of secondary lithium ion batteries and their manufacture"
- SUN Y -K ET AL: "SYNTHESIS OF ULTRAFINE LICOO2 POWDERS BY THE SOL-GEL METHOD" JOURNAL OF MATERIALS SCIENCE,GB,CHAPMAN AND HALL LTD. LONDON, vol. 31, no. 14, 15 July 1996 (1996-07-15), pages 3617-3621, XP000599896 ISSN: 0022-2461

EP 1 137 598 B1

Printed by Jouve, 75001 PARIS (FR)

Description

Field of the Invention

[0001] The present invention relates to lithium metal oxides for use as positive electrode materials for lithium and lithium-ion secondary batteries, and to methods of making lithium metal oxides.

Background of the Invention

[0002] Lithium metal oxides of the formula $LiMO_2$, wherein M is a transition metal, are important cathode (positive electrode) materials for rechargeable lithium and lithium-ion batteries. Examples of $LiMO_2$ compounds include $LiCoO_2$, $LiNiO_2$, and $LiMnO_2$. Presently, $LiCoO_2$ is used in most commercial lithium and lithium-ion batteries as a cathode material.

[0003] $LiMO_2$ compounds can have different crystal structures and phases, even within the same compound. For example, $LiCoO_2$ synthesized at greater than 700°C has a hexagonal layered structure analogous to α-$NaFeO_2$. $LiCoO_2$ synthesized at around 400°C, however, has a cubic spinel-like structure analogous to $Li_2Ti_2O_4$. Both structures have essentially the same FCC (face centered cubic) closed packed arrangement for oxygen except the layered structure has a small distortion in the direction perpendicular to the layers. Additionally, the two structures differ in cation arrangement.

[0004] It has been determined that the cubic spinel-like $LiCoO_2$ turns into hexagonal layered $LiCoO_2$ when heated to temperatures above 700°C. Therefore, phase transformation between the two structures is possible and the layered structure is energetically favored only at high temperatures. Layered $LiCoO_2$ also has an energetically favored tendency of changing into spinel $LiCo_2O_4$ when 50% of the lithium ions are removed from the $LiCoO_2$ during electrochemical charging. See A. van der Ven et al., Phys, Rev. B 58, 2975 (1998); and H. Wang et al., J. Electrochem. Soc., 146, 473 (1999). The spinel-like $LiCoO_2$ and spinel $LiCo_2O_4$ also have essentially the same atom arrangement except that lithium is at the octahedral 16c site in spinel-like $LiCoO_2$ and at tetrahedral 8a site in spinel $LiCo_2O_4$.

[0005] The tendency of the phase transformation from hexagonal layered $LiMO_2$ to cubic spinel-like $LiMO_2$ is not unique to $LiCoO_2$. Layered $LiMnO_2$ also turns into spinel-like $LiMnO_2$ only after a few cycles in an electrochemical cell. Although a cubic spinel-like $LiNiO_2$ has not been experimentally observed, $Li_{0.5}NiO_2$ (50% delithiated $LiNiO_2$) will indeed turn into $LiNi_2O_4$ spinel.

[0006] The electrochemical performance of $LiMO_2$ compounds having a cubic spinel-like structure has been found to be particularly poor, especially compared to layered structures. Moreover, the mere presence of the cubic spinel-like structural phase within the layered phase or on the surface of the layered phase has also been found to be detrimental to battery performance. In particular, the presence of cubic spinel-like phases within the layered crystal structure impedes the diffusion of lithium ions during the charge and discharge cycles of the rechargeable lithium or lithium-ion battery. Furthermore, because the cubic spinel-like phase is energetically favored and only kinetic limitations prevent large scale phase transformation, the presence of localized cubic spinel-like structures can act as a seed for phase transformation to readily occur in the $LiMO_2$ compound. Therefore, even the minor presence of cubic spinel-like phases, even at levels that cannot be detected by bulk techniques, such as powder x-ray diffraction (XRD), can cause problems in battery cycling.

Summary of the Invention

[0007] The present invention provides lithium metal oxides that are substantially single-phase compounds having hexagonal layered crystal structures that are substantially free of localized cubic spinel-like structural phases. Therefore, the lithium metal oxides of the invention have more consistent electrochemical performance than prior art compounds. In addition, the lithium metal oxide compounds of the invention have good structural stability and maintain their structure through cycling. Therefore, the lithium metal oxides of the invention are useful for rechargeable lithium and lithium ion secondary batteries.

[0008] The lithium metal oxides of the invention have the formula $Li_\alpha M_\beta A_\gamma O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90 \leq \alpha \leq 1.10$ and $\beta + \gamma = 1$. As measured using powder x-ray diffraction, the $Li_\alpha M_\beta A_\gamma O_2$ compounds according to the invention preferably have no diffraction peaks at a smaller scattering angle than the diffraction peak corresponding to Miller indices (003). In addition, the ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (110) to the integrated intensity of the diffraction peak corresponding to Miller indices (108) using powder x-ray diffraction is preferably greater than or equal to 0.7, more preferably greater than or equal to 0.8. The ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (102) to the integrated intensity of the diffraction peak corresponding to Miller indices (006) using powder x-ray diffraction is preferably greater than or equal to 1.0, more preferably greater than or equal to 1.2. The average oxidation state of the dopants N is preferably about +3.

[0009] In one preferred embodiment of the invention, the $Li_\alpha M_\beta A_\gamma O_2$ compound is $LiCoO_2$. As measured using electron paramagnetic resonance, the $LiCoO_2$ compounds of the invention typically have a change in intensity from the peak at about g = 12 to the valley at about g = 3 of greater than 1 standard weak pitch unit, and more typically of greater than 2 standard weak pitch

units.

[0010] In addition to the $Li_\alpha M_\beta A_\gamma O_2$ compounds above, the present invention is also directed to the delithiated forms of these compounds resulting from the electrochemical cycling of these compounds. Specifically, the present invention includes $Li_{\alpha-x}M_\beta A_\gamma O_2$ compounds wherein $0\leq x\leq\alpha$ that are derived by electrochemically removing x Li per formula unit from a compound having the formula $Li_\alpha M_\beta A_\gamma O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90\leq\alpha\leq1.10$ and $\beta + \gamma = 1$. The $Li_{\alpha-x}M_\beta A_\gamma O_2$ compounds are substantially single-phase lithium metal oxide compounds having hexagonal layered crystal structures that are substantially free of localized cubic spinel-like structural phases.

[0011] The present invention further includes lithium and lithium ion secondary batteries including a positive electrode comprising a compound having the formula $Li_\alpha M_\beta A_\gamma O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90\leq\alpha\leq1.10$ and $\beta + \gamma = 1$. The $Li_\alpha M_\beta A_\gamma O_2$ compound used in the positive electrode has a substantially single phase, hexagonal layered crystal structure and is substantially free of localized cubic spinel-like structural phases.

[0012] The present invention further includes a method of preparing compounds having a substantially single phase, hexagonal layered crystal structure that are substantially free of localized cubic spinel-like structural phases. A lithium metal oxide having the formula $Li_\alpha M_\beta A_\gamma O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90\leq\alpha\leq1.10$ and $\beta + \gamma = 1$, is provided at a temperature of at least about 600°C, and preferably of greater than 800°C. The lithium metal oxide is then cooled at a rate of greater than 8°C/min, preferably between 8°C/min and 140°C/min, more preferably between 10°C/min and 100°C/min. The lithium metal oxide can be synthesized at a temperature of at least about 600°C, and preferably of greater than 800°C, and then cooled at these rates, or the lithium metal oxide can be previously synthesized, heated to a temperature of at least about 600°C, and preferably of greater than 800°C, and then cooled at these rates. The lithium metal oxide is preferably uniformly cooled to provide homogeneity throughout the material being produced.

[0013] In a preferred method embodiment of the invention, the $Li_\alpha M_\beta A_\gamma O_2$ compound is $LiCoO_2$ and is prepared by the method of the invention using a lithium source compound and a cobalt source compound. In particular, the preferred lithium source compound is selected from the group consisting of Li_2CO_3 and LiOH and the preferred cobalt source compound is selected from the group consisting of Co_3O_4 and $Co(OH)_2$. More preferably, the $LiCoO_2$ is prepared from Li_2CO_3 and Co_3O_4.

[0014] These and other features and advantages of the present invention will become more readily apparent to those skilled in the art upon consideration of the following detailed description and accompanying drawings, which describe both the preferred and alternative embodiments of the present invention.

Brief Description of the Drawings

[0015] Fig. 1 is a graph comparing the cycle performance between a comparative compound (sample 1) and a compound according to the invention (sample 2).

[0016] Fig. 2 is a graph illustrating the electron paramagnetic resonance (EPR) spectrum of a weak pitch standard sample with a correction factor of 1.14.

[0017] Fig. 3 is a graph illustrating the EPR spectrum of a comparative compound (sample 1).

[0018] Fig. 4 is a graph illustrating the EPR spectrum of a compound according to the invention (sample 2).

[0019] Fig. 5 is a graph illustrating thermogravimetric analysis (TGA) curves for a comparative compound (sample 1) and a compound according to the invention (sample 2).

[0020] Fig. 6 is a powder x-ray diffraction pattern for a compound according to the invention (sample 2) using Cu Kα radiation.

[0021] Fig. 7 is a graph comparing the cycle performance of a comparative compound (sample 3) and a compound according to the invention (sample 4).

Detailed Description of the Preferred Embodiments of the Invention

[0022] In the drawings and the following detailed description, preferred embodiments are described in detail to enable practice of the invention. Although the invention is described with reference to these specific preferred embodiments, it will be understood that the invention is not limited to these preferred embodiments. But to the contrary, the invention includes numerous alternatives, modifications and equivalents as will become apparent from consideration of the following detailed description and accompanying drawings.

[0023] The present invention is directed to substantially single-phase lithium metal oxide compounds having hexagonal layered crystal structures that are substantially free of localized cubic spinel-like structural phases on the surface of the crystal or within the crystal. The lithium metal oxides of the invention have the formula $Li_\alpha M_\beta A_\gamma O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90\leq\alpha\leq1.10$, $\beta > 0$, $\gamma \geq 0$ and $\beta + \gamma = 1$. Preferably, the transition metal M is Ni, Co, Mn, or combinations thereof.

[0024] The dopants A are elements other than M selected to produce an oxidation state N wherein $+2.5 \leq N \leq +3.5$, and preferably N is about 3. As would be readily understood by those skilled in the art, the average

oxidation state N is based on the molar amounts of the dopants used and the valences of the dopants used. For example, if the dopants are 40% Ti^{4+} and 60% Mg^{2+}, on a molar basis, the average oxidation state N would be $(0.4)(+4) + (0.6)(+2) = +2.8$.

[0025] As defined above, the dopants A are used to replace the transition metal M and are not used to take the place of lithium ions in the lithium metal oxide, i.e., $\beta = 1 - \gamma$. Therefore, the reversible capacity is maximized in the intercalation compounds of the invention. Exemplary dopants for use in the invention include metals and non-metals such as Ti, Zr, Mg, Ca, Sr, Ba, Al, Ga, Si, Ge, Sn and combinations thereof. For example, A can include equal amounts of dopants Ti^{4+} and Mg^{2+}. Typically, in the compounds of the invention, γ is greater than or equal to 0 and less than about 0.5.

[0026] The substantially single-phase, hexagonal layered structures of the compounds of the invention can be characterized, for example, by their powder x-ray diffraction patterns. Typically, as measured using powder x-ray diffraction, the $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ compounds according to the invention preferably have no diffraction peaks at a smaller scattering angle than the diffraction peak corresponding to Miller indices (003) thereby demonstrating that the compounds of the invention are substantially single phase. In addition, the ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (110) to the integrated intensity of the diffraction peak corresponding to Miller indices (108) using powder x-ray diffraction is preferably greater than or equal to 0.7, more preferably greater than or equal to 0.8. The ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (102) to the integrated intensity of the diffraction peak corresponding to Miller indices (006) using powder x-ray diffraction is preferably greater than or equal to 1.0, more preferably greater than or equal to 1.2. The integrated intensities for these measurements is based on the area measured below the respective peaks. Alternatively, the heights of the peaks can be used to provide a rough comparison of the integrated intensities and because the widths of the peaks are relatively uniform, the ratios of peak heights are approximately equal to the ratios of the integrated intensities for the two peaks being compared.

[0027] In one preferred embodiment of the invention, the $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ compound is $LiCoO_2$. As measured using electron paramagnetic resonance, the $LiCoO_2$ compounds of the invention typically have a change in intensity from the peak at about g = 12 to the valley at about g = 3 of greater than 1 standard weak pitch unit, and more typically of greater than 2 standard weak pitch units. In particular, Fig. 4, which is discussed in more detail in the examples, illustrates the change of intensity in this region of the EPR graph.

[0028] Furthermore, although $LiCoO_2$ is described as preferred, the present invention applies to compounds of the formula $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ other than $LiCoO_2$. In particular, as would be readily understood by those skilled in the art, the other lithium metal oxides of the above formula (e.g., wherein M is Ni or Mn) have a layered crystal structure similar to $LiCoO_2$. Therefore, the present invention applies to these $LiMO_2$ compounds in general and suppressing the formation or transformation of the cubic spinel-like phases within the crystal or on the surface of the crystal, thereby enhancing the performance of the material in a lithium or lithium-ion secondary battery.

[0029] The present invention further includes a method of preparing compounds having a substantially single phase, hexagonal layered crystal structure that are substantially free of localized cubic spinel-like structural phases. In accordance with this method, a lithium metal oxide is provided having the formula $Li_{\alpha}M_{\beta}A_{\gamma}O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90 \leq \alpha \leq 1.10$ and $\beta + \gamma = 1$, at a temperature of at least about 600°C, and preferably of greater than 800°C. The lithium metal oxide can be provided at these temperatures by either synthesizing the material at these temperatures or by heating previously synthesized material.

[0030] The lithium metal oxide compounds of the invention can be prepared or synthesized by mixing together stoichiometric amounts of source compounds containing lithium, M and A to give the desired molar ratio for the formula $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ described above. The source compounds (raw materials) can be the pure elements but are typically compounds containing the elements such as oxides or salts thereof. For example, the source compounds are typically hydrated or anhydrous oxides, hydroxides, carbonates, nitrates, sulfates, chlorides or fluorides, but can be any other suitable source compound that will not cause elemental defects in the resulting lithium metal oxide compound. The elements for the lithium metal oxide compound can each be supplied from separate source compounds or at least two of the elements can be supplied from the same source compounds. In addition, the source compounds can be mixed in any desirable order.

[0031] Although the lithium metal oxide compounds are preferably prepared by solid state reactions, it can be advantageous to react the raw materials using wet chemistry such as sol-gel type reactions or spray drying techniques, alone or in combination with solid state reactions. For example, the source compounds comprising the M and A can be prepared as a solution in a solvent such as water and the M and A precipitated out of solution as an intimately mixed compound such as a hydroxide. The mixed compound can then be blended with a lithium source compound. The reaction mixture can also be prepared by suspending source compounds in a solution of other source compounds and spray drying the resulting slurry to obtain an intimate mixture. Typically, the selection of reaction methods will vary depending on the raw materials used and the desired end product.

[0032] In a preferred method embodiment of the invention, wherein M is Co, the lithium metal oxide (e.g. $LiCoO_2$) is prepared using a lithium source compound and a cobalt source compound. In particular, the preferred lithium source compound is selected from the group consisting of Li_2CO_3 and LiOH and the preferred cobalt source compound is selected from the group consisting of Co_3O_4 and $Co(OH)_2$. More preferably, the $LiCoO_2$ is prepared from Li_2CO_3 and Co_3O_4.

[0033] The mixture once prepared can be reacted to form the lithium metal oxide. Preferably, the mixture is reacted by firing the mixture at a temperature between 600°C and 1000°C for sufficient time to produce the lithium metal oxide compound in a single phase. The mixture is generally fired for a total of between about 4 and about 48 hours in one or more firing steps. Any suitable apparatus can be used for firing the mixture, such as a rotary calciner, a stationary furnace or a tunnel furnace, that uniformly heats the source compounds to produce the lithium metal oxide.

[0034] Once the lithium metal oxide is at its final preparation temperature or after previously synthesized lithium metal oxide has been reheated, the lithium metal oxide is cooled at a rate of greater than 8°C/min, preferably between 8°C/min and 140°C/min, more preferably between 10°C/min and 100°C/min. It has been discovered that cooling at a rate of greater than 140°C/min results in a structure with high crystalline stress and strain that does not have the strength of lithium metal oxides cooled at a rate of between 8°C/min and 140°C/min. Moreover, it has been discovered that cooling at a rate of less than 8°C/min results in the formation of localized cubic spinel-like structural phases on the surface of the crystal or within the crystal and thus decreased electrochemical performance. With the lithium metal oxides of the invention, the lack of localized hetero-structural phases, e.g., cubic spinel-like phases, within the crystal and on the crystal surface does not induce further phase transformation that impedes the diffusion of the Li^+ ions during the charge and discharge cycles. Thus, the hexagonal layered compounds of the invention have better and more consistent electrochemical performance than prior art compounds that are cooled at slower rates.

[0035] The lithium metal oxide is preferably uniformly cooled (quenched) in accordance with the invention. In particular, the lithium metal oxide material is preferably cooled at approximately the same rate. For example, the variation between the mean cooling rate and the cooling rate for any specific portion of the material should be less than about 10 percent. In a preferred embodiment of the invention, uniform cooling can be accomplished using a rotary calciner, or a stationary furnace or tunnel furnace with smaller bed depths. The uniformly cooled material prepared according to the invention has greater homogeneity and less variance in its material properties than material that is not uniformly cooled.

[0036] The present invention further includes lithium and lithium ion secondary batteries that include a positive electrode comprising the lithium metal oxides of the invention. Typically, the lithium metal oxide compound of the invention is combined with a carbonaceous material and a binder polymer to form a cathode. The negative electrode of the lithium battery can be lithium metal or alloys, or any material capable of reversibly lithiating and delithiating at an electrochemical potential relative to lithium metal between about 0.0 V and 0.7 V. Examples of negative electrode materials include carbonaceous materials containing H, B, Si and Sn; tin oxides; tin-silicon oxides; and composite tin alloys. The negative electrode is separated from the positive electrode material in the cell using an electronic insulating separator. The electrochemical cell further includes an electrolyte. The electrolyte can be non-aqueous liquid, gel or solid and preferably comprises a lithium salt, e.g., $LiPF_6$. Electrochemical cells using the lithium metal oxide compounds of the invention as positive electrode material can be combined for use in portable electronics such as cellular phones, camcorders; and laptop computers, and in large power applications such as for electric vehicles and hybrid electric vehicles.

[0037] The lithium metal oxide compounds of the invention allow lithium ions to readily diffuse during both the charge and discharge cycles of the battery. In particular, in the discharge cycle for these lithium metal oxides wherein x Li per formula unit are electrochemically removed per formula unit, the lithium metal oxide takes the formula $Li_{\alpha-x}M_{\beta}A_{\gamma}O_2$, wherein $0 \leq x \leq \alpha$.

[0038] The lithium metal oxide compounds of the invention have been found to have good initial specific capacities and good cycleability as is desired in the art. For example, the initial specific capacity of the $LiCoO_2$ of the invention is greater than 140 mAh/g, preferably greater than 150 mAh/g. In addition, the capacity loss over 100 cycles for the lithium metal oxides of the invention is less than 25%, preferably less than 20%, with a constant current of C/3 (3 hours for complete charge or discharge) when cycled between 3.0 and 4.3 V versus lithium.

[0039] The present invention will now be further demonstrated by the following non-limiting examples.

EXAMPLE 1

[0040] A commercial $LiCoO_2$ sample (sample 1) was heated to 950°C for 1 hour and then quench cooled by taking the sample directly from the hot zone and spreading the sample onto a stainless steel pan at room temperature. The cooling time was estimated at about 10 minutes from 950°C to room temperature. Sample 1 and the quenched sample (sample 2) were used as positive electrode materials for different electrochemical cells, each cell using a coin cell configuration with Li metal as the negative electrode. NRC 2325 coin cell hardware and Celgard 3501 separators were used. The electrolyte was 1M $LiPF_6$ in a 50:50 mixture of ethylene car-

bonate and dimethyl carbonate solvents. The positive electrode consisted of 85% active material (by weight), 10% super S™ carbon black and 5% polyvinylidene fluoride (PVDF) as a binder polymer, coated on aluminum foil. The cycle tests were conducted between 3.0 and 4.3 V using a constant current of C/3 (3 hours for complete charge or discharge) in both charge and discharge.

[0041] Fig. 1 compares the cycle performance of sample 1 and sample 2. As shown in Fig. 1, sample 2 retains more capacity upon cycling than sample 1 and has much improved cycle performance over sample 1.

[0042] In addition, electron paramagnetic resonance (EPR) spectra of sample 1 and sample 2 were obtained using a Bruker Instruments EMX system. The sweep of the magnetic field was from 100 to 5100 Gauss, and the microwave frequency was fixed at 9.85 GHz. A Bruker Instruments' weak pitch standard (0.0035% pitch in KCl) with a correction factor of 1.14 was used to calibrate the intensity. Fig. 2 shows the EPR spectrum from this standard. The intensity of the carbon feature from this standard, as shown in Fig. 2, is defined as 1.14 standard weak pitch units.

[0043] The $LiCoO_2$ samples (sample 1 and sample 2) were directly packed into EPR tubes without dilution for the measurement. The resulting EPR spectra of samples 1 and 2 are shown in Figs. 3 and 4, respectively. The sharp feature in both Figs. 3 and 4 at around g=2.14 is due to nickel impurities. The broad feature from about g = 14 to about g =2.5 in Fig. 4 is due to the high spin cobalt that is characteristic of the $LiCoO_2$ prepared according to the invention.

[0044] Thermogravimetric analysis (TGA) of samples 1 and 2 were also conducted. As shown in Fig. 5, neither sample 1 nor sample 2 has any significant weight loss in the range of 650 to 900°C.

[0045] Sample 2 prepared according to the invention was further tested using powder x-ray diffraction with Cu Kα radiation to determine if this material had a substantially single-phase, hexagonal layered structure. As shown in Fig. 6, sample 2 has a ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (110) to the integrated intensity of the diffraction peak corresponding to Miller indices (108) using powder x-ray diffraction greater than or equal to 0.7, a ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (102) to the integrated intensity of the diffraction peak corresponding to Miller indices (006) using powder x-ray diffraction greater than or equal to 1.0, and no diffraction peaks using powder x-ray diffraction at a smaller scattering angle than the diffraction peak corresponding to Miller indices (003), as desired in accordance with the invention.

EXAMPLE 2

[0046] Stoichiometric amounts of Li_2CO_3 and Co_3O_4 were mixed and then heated at a rate of 3.75°C/min from room temperature to 950°C, held at 950°C for 5 hours, and then cooled to room temperature at a rate of about 3.7°C/min (total cooling time slightly longer than 4 hours). The resulting compound is sample 3.

[0047] Stoichiometric amounts of Li_2CO_3 and Co_3O_4 were mixed and then heated at a rule of 3.75°C/min from room temperature to 950°C, held at 950°C for 5 hours, and then cooled to loom temperature at a rate of about 8°C/min (total cooling time just under 2 hours). The resutling compound is sample 4.

[0048] Samples 3 and 4 were cycle tested according to the method described in Example 1. Fig. 7 compares the cycle performance of sample 3 and sample 4. As shown in Fig. 7, sample 4 prepared according to the invention has better cycling performance than sample 3.

Claims

1. A compound having the formula $Li_\alpha M_\beta A_\gamma O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90 \leq \alpha \leq 1.10$ and $\beta + \gamma = 1$, said compound having a substantially single phase, hexagonal layered crystal structure and being substantially free of localized cubic spinel-like structural phases.

2. A compound having the formula $Li_{\alpha-x}M_\beta A_\gamma O_2$, wherein $0 \leq x \leq \alpha$, said compound derived by electrochemically removing x Li per formula unit from a compound having the formula $Li_\alpha M_\beta A_\gamma O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90 \leq \alpha \leq 1.10$ and $\beta + \gamma = 1$, said compound having a substantially single phase, hexagonal layered crystal structure and being substantially free of localized cubic spinel-like structural phases.

3. The compound according to Claim 1 or 2, wherein, in the powder x-ray diffraction pattern, there are no diffraction peaks at a smaller scattering angle than the diffraction peak corresponding to Miller indices (003).

4. The compound according to any of the preceding claims, wherein the ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (110) to the integrated intensity of the diffraction peak corresponding to Miller indices (108) using powder x-ray diffraction is greater than or equal to 0.7.

5. The compound according to any of the preceding claims, wherein the ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (110) to the integrated intensity of the diffraction

peak corresponding to Miller indices (108) using powder x-ray diffraction is greater than or equal to 0.8.

6. The compound according to any of the preceding claims, wherein the ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (102) to the integrated intensity of the diffraction peak corresponding to Miller indices (006) using powder x-ray diffraction is greater than or equal to 1.0.

7. The compound according to any of the preceding claims, wherein the ratio of the integrated intensity of the diffraction peak corresponding to Miller indices (102) to the integrated intensity of the diffraction peak corresponding to Miller indices (006) using powder x-ray diffraction is greater than or equal to 1.2.

8. The compound according to any of the preceding claims having the formula $LiCoO_2$.

9. The compound according to Claim 8, wherein the intensity change from the peak at about g = 12 to the valley at about g = 3 using electron paramagnetic resonance is greater than 1 standard weak pitch unit.

10. The compound according to Claim 8, wherein the intensity change from the peak at about g = 12 to the valley at about g = 3 using electron paramagnetic resonance is greater than 2 standard weak pitch units.

11. The compound according to any of the preceding claims, wherein the average oxidation state N of the dopants is about +3.

12. A lithium or lithium ion secondary battery including a positive electrode comprising the compound of any of the preceding claims.

13. A method of preparing a compound having a substantially single phase, hexagonal layered crystal structure and being substantially free of localized cubic spinel-like structural phases, the method comprising the steps of providing a lithium metal oxide having the formula $Li_{\alpha}M_{\beta}A_{\gamma}O_2$, wherein M is one or more transition metals, A is one or more dopants having an average oxidation state N such that $+2.5 \leq N \leq +3.5$, $0.90 \leq \alpha \leq 1.10$ and $\beta + \gamma = 1$, at a temperature of at least about 600°C; and cooling the compound at a rate of greater than 8°C/min.

14. The method according to Claim 13, wherein said cooling step comprises cooling the compound at a rate of greater than 10°C/min.

15. The method according to Claim 13, wherein said cooling step comprises cooling the compound at a rate of between 8°C/min and 140°C/min.

16. The method according to Claim 13, wherein said cooling step comprises cooling the compound at a rate of between 10°C/min and 90°C/min.

17. The method according to any of Claims 13-16, wherein said providing step comprises provided in the $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ compound at a temperature of at least about 800°C.

18. The method according to any of Claims 13-17, wherein said cooling step comprises uniformly cooling the $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ compound.

19. The method according to any of Claims 13-18, wherein said providing step comprises synthesizing the $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ compound at a temperature of at least about 600°C.

20. The method according to any of Claims 13-18, wherein said providing step comprising heating a previously-synthesized $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ compound to a temperature of at least about 600°C.

Patentansprüche

1. Verbindung mit der Formel $Li_{\alpha}M_{\beta}A_{\gamma}O_2$, worin M ein oder mehrere Übergangsmetalle darstellt, A ein oder mehrere Dotiermittel mit einem mittleren Oxidationszustand N darstellt derart, dass $+2,5 \leq N \leq +3,5$, $0,90 \leq \alpha \leq 1,10$ und $\beta + \gamma = 1$, wobei die Verbindung eine im wesentlichen einphasige, hexagonale, geschichtete Kristallstruktur aufweist und im wesentlichen frei von lokalen kubischen, Spinell-artigen Strukturphasen ist.

2. Verbindung mit der Formel $Li_{\alpha-x}M_{\beta}A_{\gamma}O_2$, worin $0 \leq x \leq \alpha$, wobei die Verbindung durch elektrochemisches Entfernen von x Li pro Formeleinheit von einer Verbindung mit der Formel $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ abgeleitet ist, wobei M ein oder mehrere Übergangsmetalle darstellt, A ein oder mehrere Dotiermittel mit einem mittleren Oxidationszustand N darstellt derart, dass $+2,5 \leq N \leq +3,5$, $0,90 \leq \alpha \leq 1,10$ und $\beta + \gamma = 1$, wobei die Verbindung eine im wesentlichen einphasige, hexagonale, geschichtete Kristallstruktur aufweist und im wesentlichen frei von lokalen kubischen, Spinell-artigen Strukturphasen ist.

3. Verbindung nach Anspruch 1 oder 2, worin im Pulver-Röntgenbeugungsspektrum keine Beugungspeaks bei einem kleineren Streuwinkel als dem Beugungspeak, der den Millerschen Indices (003) entspricht, vorliegen.

4. Verbindung nach irgendeinem der vorhergehenden Ansprüche, worin das Verhältnis der integrierten Intensität des den Millerschen Indices (110) entsprechenden Beugungspeaks zur integrierten Intensität des den Millerschen Indices (108) entsprechenden Beugungspeaks bei Anwendung einer Pulver-Röntgenbeugung größer als oder gleich 0,7 ist.

5. Verbindung nach irgendeinem der vorhergehenden Ansprüche, worin das Verhältnis der integrierten Intensität des den Millerschen Indices (110) entsprechenden Beugungspeaks zur integrierten Intensität des den Millerschen Indices (108) entsprechenden Beugungspeaks bei Anwendung einer Pulver-Röntgenbeugung größer als oder gleich 0,8 ist.

6. Verbindung nach irgendeinem der vorhergehenden Ansprüche, worin das Verhältnis der integrierten Intensität des den Millerschen Indices (102) entsprechenden Beugungspeaks zur integrierten Intensität des den Millerschen Indices (006) entsprechenden Beugungspeaks bei Anwendung einer Pulver-Röntgenbeugung größer als oder gleich 1,0 ist.

7. Verbindung nach irgendeinem der vorhergehenden Ansprüche, worin das Verhältnis der integrierten Intensität des den Millerschen Indices (102) entsprechenden Beugungspeaks zur integrierten Intensität des den Millerschen Indices (006) entsprechenden Beugungspeaks bei Anwendung einer Pulver-Röntgenbeugung größer als oder gleich 1,2 ist.

8. Verbindung nach irgendeinem der vorhergehenden Ansprüche mit der Formel $LiCoO_2$.

9. Verbindung nach Anspruch 8, worin die Intensitätsänderung vom Peak bei etwa g = 12 zum Tal bei etwa g = 3 bei Anwendung elektronenparamagnetischer Resonanz größer als 1 Standard-"Weak-Pitch"-Einheit ist.

10. Verbindung nach Anspruch 8, worin die Intensitätsänderung vom Peak bei etwa g = 12 zum Tal bei etwa g = 3 bei Anwendung elektronenparamagnetischer Resonanz größer als 2 Standard-"Weak-Pitch"-Einheiten ist.

11. Verbindung nach irgendeinem der vorhergehenden Ansprüche, worin der mittlere Oxidationszustand N der Dotiermittel etwa +3 beträgt.

12. Lithium- oder Lithium-Ion-Akkumulator einschließlich einer positiven Elektrode umfassend die Verbindung nach irgendeinem der vorhergehenden Ansprüche.

13. Verfahren zur Herstellung einer Verbindung mit einer im wesentlichen einphasigen, hexagonalen, geschichteten Kristallstruktur, die im wesentlichen frei von lokalen kubischen, Spinell-artigen Strukturphasen ist, wobei das Verfahren die Schritte des Bereitstellens eines Lithiummetalloxids mit der Formel $Li_\alpha M_\beta A_\gamma O_2$, worin M ein oder mehrere Übergangsmetalle darstellt und A ein oder mehrere Dotiermittel mit einem mittleren Oxidationszustand N darstellt derart, dass $+2,5 \leq N \leq +3,5$, $0,90 \leq \alpha \leq 1,10$ und $\beta + \gamma = 1$, bei einer Temperatur von mindestens etwa 600°C und des Abkühlens der Verbindung mit einer Geschwindigkeit von mehr als 8°C/min umfasst.

14. Verfahren nach Anspruch 13, worin der Kühlschritt das Abkühlen der Verbindung mit einer Geschwindigkeit von mehr als 10°C/min umfasst.

15. Verfahren nach Anspruch 13, worin der Kühlschritt das Abkühlen der Verbindung mit einer Geschwindigkeit zwischen 8°C/min und 140°C/min umfasst.

16. Verfahren nach Anspruch 13, worin der Kühlschritt das Abkühlen der Verbindung mit einer Geschwindigkeit zwischen 10°C/min und 90°C/min umfasst.

17. Verfahren nach irgendeinem der Ansprüche 13 bis 16, worin der Bereitstellungsschritt die Bereitstellung der Verbindung $Li_\alpha M_\beta A_\gamma O_2$ bei einer Temperatur von mindestens etwa 800°C umfasst.

18. Verfahren nach irgendeinem der Ansprüche 13 bis 17, worin der Kühlschritt ein gleichmäßiges Abkühlen der Verbindung $Li_\alpha M_\beta A_\gamma O_2$ umfasst.

19. Verfahren nach irgendeinem der Ansprüche 13 bis 18, worin der Bereitstellungsschritt das Synthetisieren der Verbindung $Li_\alpha M_\beta A_\gamma O_2$ bei einer Temperatur von mindestens etwa 600°C umfasst.

20. Verfahren nach irgendeinem der Ansprüche 13 bis 18, worin der Bereitstellungsschritt das Erwärmen einer vorher hergestellten Verbindung $Li_\alpha M_\beta A_\gamma O_2$ auf eine Temperatur von mindestens etwa 600°C umfasst.

Revendications

1. Composé ayant la formule $Li_\alpha M_\beta A_\gamma O_2$, dans laquelle M est un ou plusieurs métaux de transition, A est un ou plusieurs dopants ayant un degré moyen d'oxydation N tel que $+ 2,5 \leq N \leq + 3,5$, $0,90 \leq \alpha \leq 1,10$ et $\beta + \gamma = 1$, ledit composé ayant une structure cristalline stratifiée hexagonale, sensiblement monophasique, et étant sensiblement exempt de phases structurales de type spinel cubiques localisées.

2. Composé ayant la formule $Li_{\alpha-x} M_\beta A_\gamma O_2$, dans la-

quelle $0 \leq x \leq \alpha$, ledit composé étant obtenu par élimination électrochimique de x Li par unité de formule à partir d'un composé ayant la formule $Li_\alpha M_\beta A_\gamma O_2$, dans laquelle M est un ou plusieurs métaux de transition, A est un ou plusieurs dopants ayant un degré moyen d'oxydation N tel que $+ 2,5 \leq N \leq + 3,5$, $0,90 \leq \alpha \leq 1,10$ et $\beta + \gamma = 1$, ledit composé ayant une structure cristalline stratifiée hexagonale, sensiblement monophasique, et étant sensiblement exempt de phases structurales de type spinel cubiques localisées.

3. Composé selon la revendication 1 ou 2, dans lequel, dans le diagramme de diffraction des rayons X par la méthode des poudres, il n'y a pas de pics de diffraction à un angle de diffusion plus petit que le pic de diffraction correspondant aux indices de Miller (003).

4. Composé selon l'une quelconque des revendications précédentes, dans lequel le rapport de l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (110) sur l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (108) par utilisation d'une diffraction des rayons X par la méthode des poudres est $\geq$ à 0,7.

5. Composé selon l'une quelconque des revendications précédentes, dans lequel le rapport de l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (110) sur l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (108) par utilisation d'une diffraction des rayons X par la méthode des poudres est $\geq$ à 0,8.

6. Composé selon l'une quelconque des revendications précédentes, dans lequel le rapport de l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (102) sur l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (006) par utilisation d'une diffraction des rayons X par la méthode des poudres est $\geq$ à 1,0.

7. Composé selon l'une quelconque des revendications précédentes, dans lequel le rapport de l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (102) sur l'intensité intégrée du pic de diffraction correspondant aux indices de Miller (006) par utilisation d'une diffraction des rayons X par la méthode des poudres est $\geq$ à 1,2.

8. Composé selon l'une quelconque des revendications précédentes, ayant la formule $LiCoO_2$.

9. Composé selon la revendication 8, dans lequel la variation d'intensité, du pic à environ g = 12 à la vallée à environ g = 3, par utilisation d'une résonance paramagnétique d'électron, est supérieure à une unité de pas faible standard.

10. Composé selon la revendication 8, dans lequel la variation d'intensité, du pic à environ g = 12 à la vallée à environ g = 3, par utilisation d'une résonance paramagnétique d'électron, est supérieure à deux unités de pas faible standard.

11. Composé selon l'une quelconque des revendications précédentes, dans lequel le degré moyen d'oxydation N des dopants est d'environ + 3.

12. Batterie secondaire au lithium ou à ion lithium, incluant une électrode positive comprenant le composé de l'une quelconque des revendications précédentes.

13. Procédé de préparation d'un composé ayant une structure cristalline stratifiée hexagonale, sensiblement monophasique, et étant sensiblement exempt de phases structurales de type spinel cubiques localisées, le procédé comprenant les étapes de mise à disposition d'un oxyde du métal lithium ayant la formule $Li_\alpha M_\beta A_\gamma O_2$, dans laquelle M est un ou plusieurs métaux de transition, A est un ou plusieurs dopants ayant un degré moyen d'oxydation N tel que $+ 2,5 \leq N \leq + 3,5$, $0,90 \leq \alpha \leq 1,10$ et $\beta + \gamma = 1$, à une température d'au moins environ 600°C ; et le refroidissement du composé à une vitesse supérieure à 8°C/mn.

14. Procédé selon la revendication 13, dans lequel ladite étape de refroidissement comprend le refroidissement du composé à une vitesse supérieure à 10°C/mn.

15. Procédé selon la revendication 13, dans lequel ladite étape de refroidissement comprend le refroidissement du composé à une vitesse comprise entre 8°C/mn et 140°C/mn.

16. Procédé selon la revendication 13, dans lequel ladite étape de refroidissement comprend le refroidissement du composé à une vitesse comprise entre 10°C/mn et 90°C/mn.

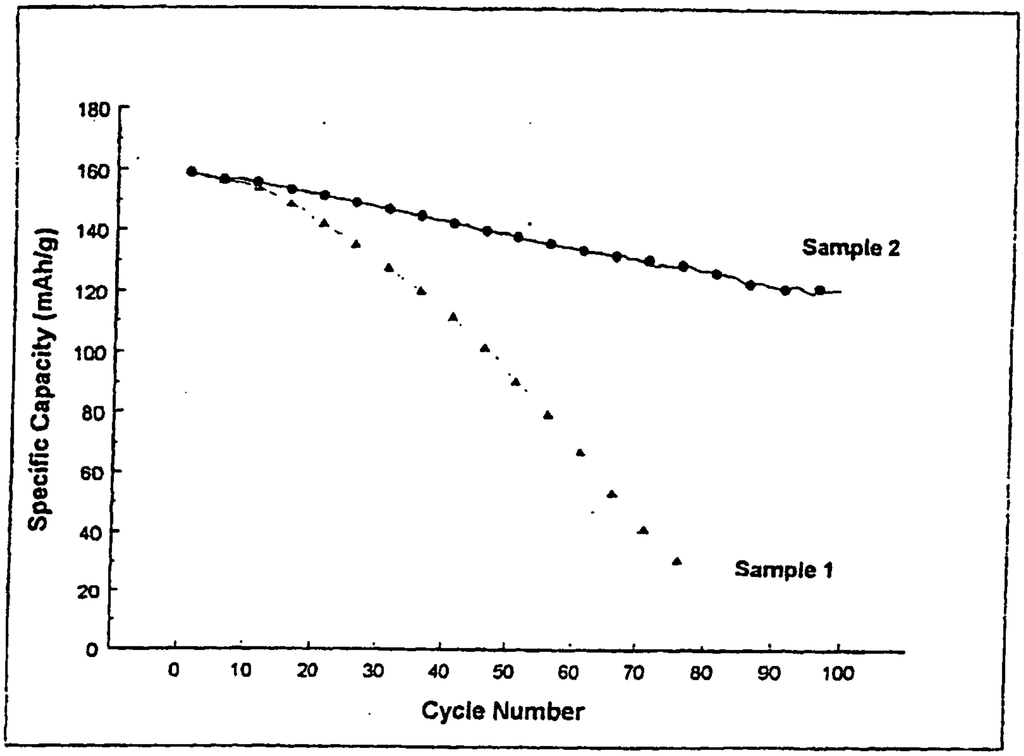
17. Procédé selon l'une quelconque des revendications 13 à 16, dans lequel ladite étape de mise à disposition comprend la mise à disposition du composé $Li_\alpha M_\beta A_\gamma O_2$ à une température d'au moins environ 800°C.

18. Composé selon l'une quelconque des revendications 13 à 17, dans lequel ladite étape de refroidissement comprend le refroidissement uniforme du composé $Li_\alpha M_\beta A_\gamma O_2$.

19. Procédé selon l'une quelconque des revendications

13 à 18, dans lequel ladite étape de mise à disposition comprend la synthèse du composé $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ à une température d'au moins environ 600°C.

20. Procédé selon l'une quelconque des revendications 13 à 18, dans lequel ladite étape de mise à disposition comprend le chauffage à une température d'au moins environ 600°C d'un composé $Li_{\alpha}M_{\beta}A_{\gamma}O_2$ préalablement synthétisé.



180
160
140
120
100
80
60
40
20
0
Specific Capacity (mAh/g)
0
10
20
30
40
50
60
70
80
90
100
Cycle Number
Sample 2
Sample 1

Fig. 1

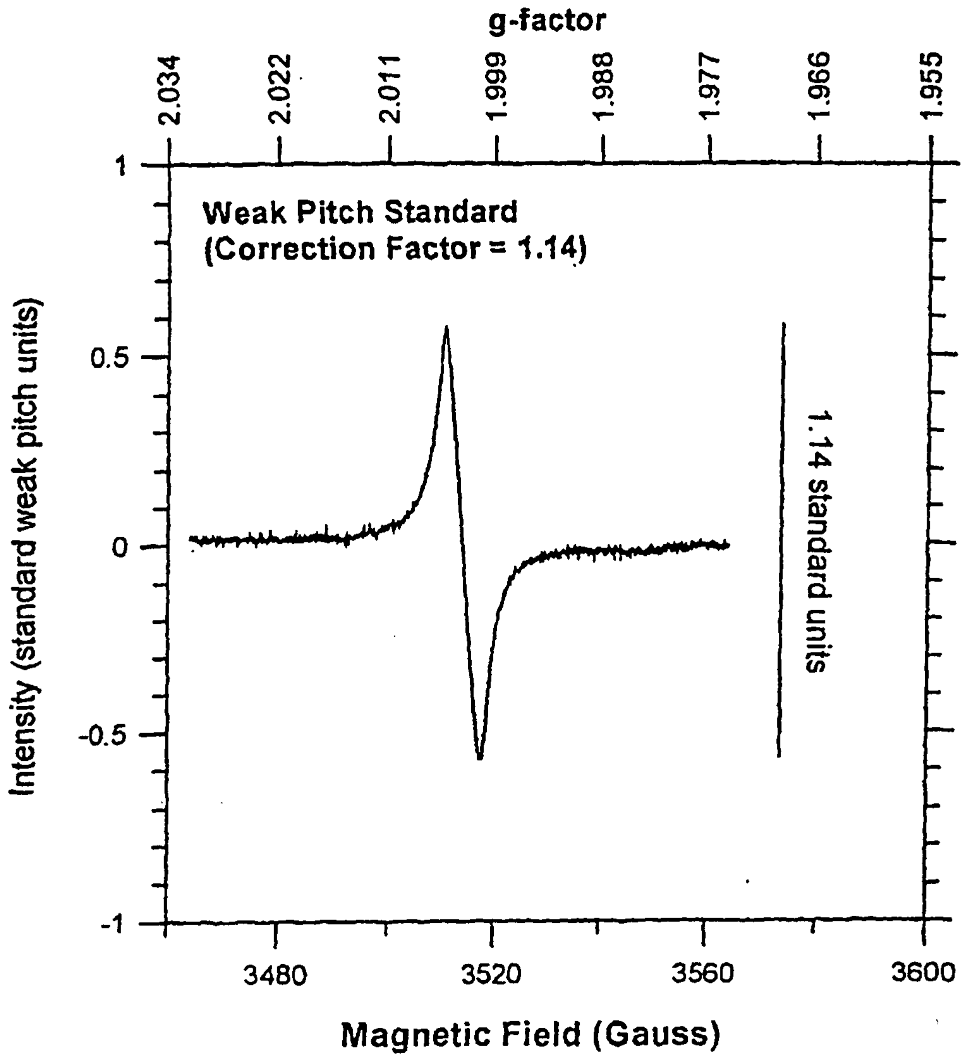

g-factor
2.034
2.022
2.011
1.999
1.988
1.977
1.966
1.955
Weak Pitch Standard
(Correction Factor = 1.14)
1.14 standard units
Intensity (standard weak pitch units)
1
0.5
0
-0.5
-1
3480
3520
3560
3600
Magnetic Field (Gauss)

Fig. 2

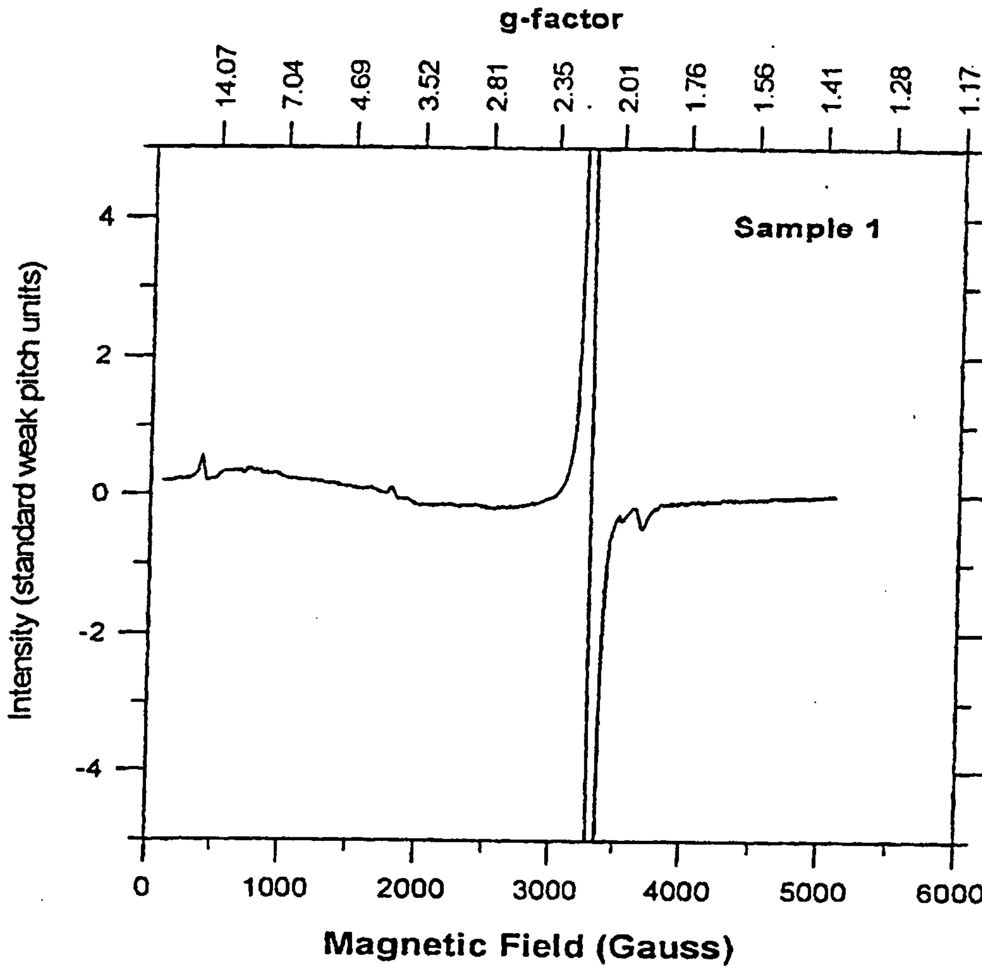

g-factor
14.07
7.04
4.69
3.52
2.81
2.35
2.01
1.76
1.56
1.41
1.28
1.17
Sample 1
Intensity (standard weak pitch units)
4
2
0
-2
-4
0
1000
2000
3000
4000
5000
6000
Magnetic Field (Gauss)

Fig. 3

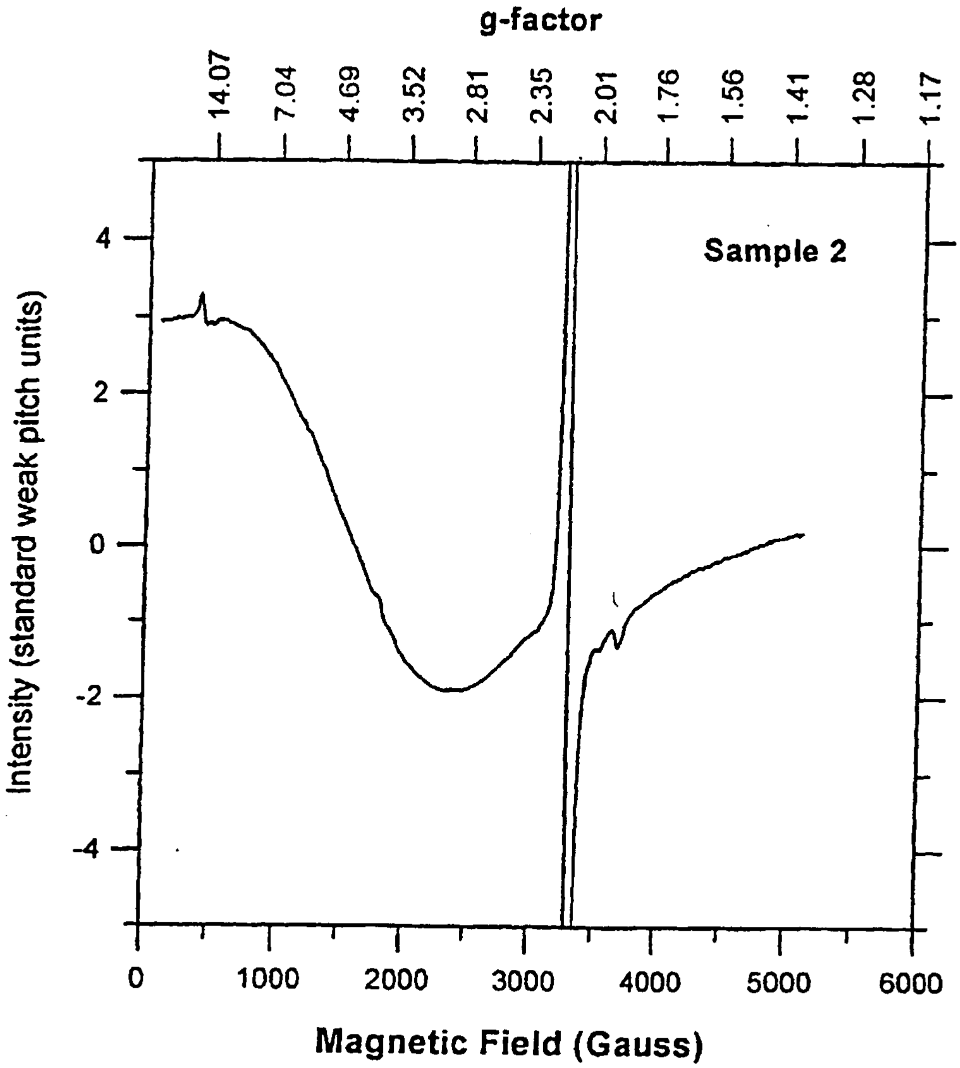

g-factor
14.07
7.04
4.69
3.52
2.81
2.35
2.01
1.76
1.56
1.41
1.28
1.17
Sample 2
Intensity (standard weak pitch units)
4
2
0
-2
-4
0
1000
2000
3000
4000
5000
6000
Magnetic Field (Gauss)

Fig. 4

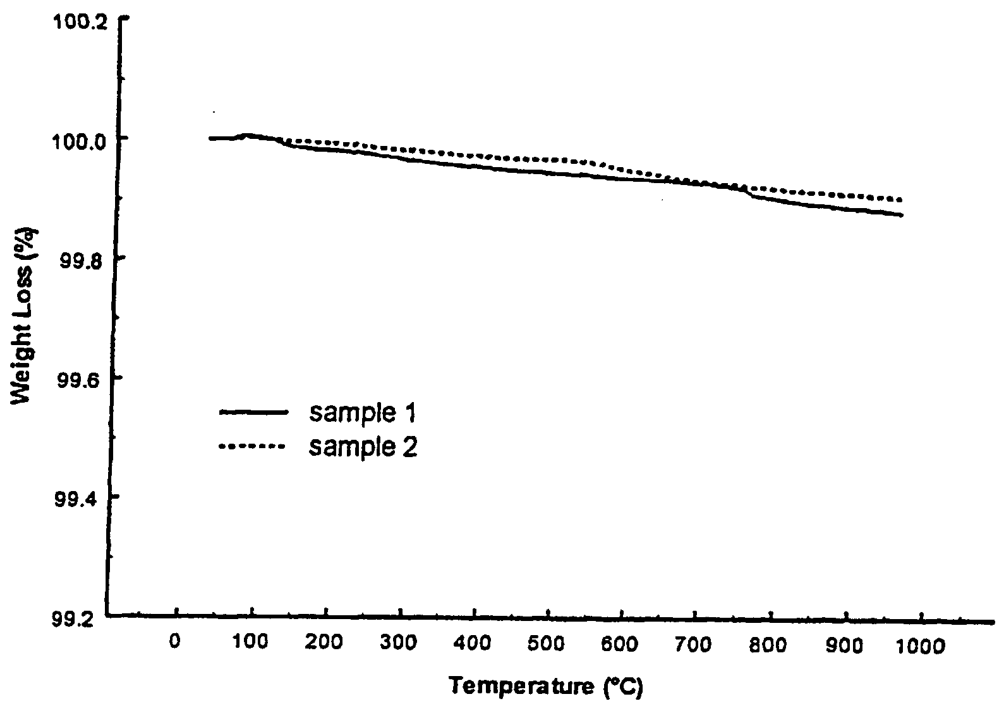
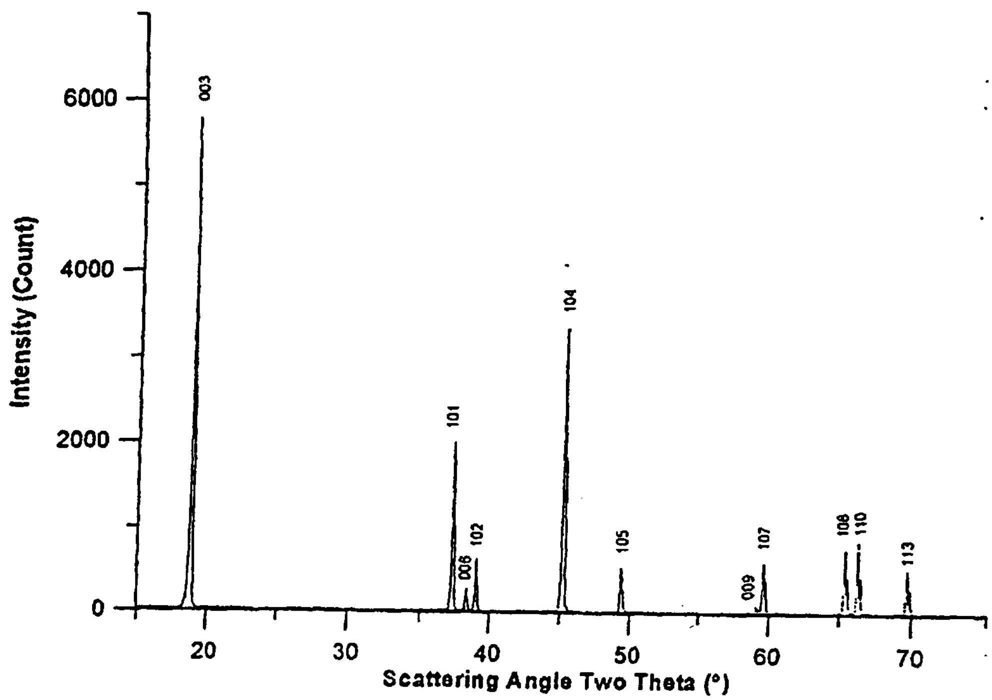

100.2
100.0
99.8
99.6
99.4
99.2
Weight Loss (%)
sample 1
sample 2
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

Fig. 5



XRD pattern of sample 2 measured with Cu Kα radiation. Miller indices are labeled on each peak.

Fig. 6

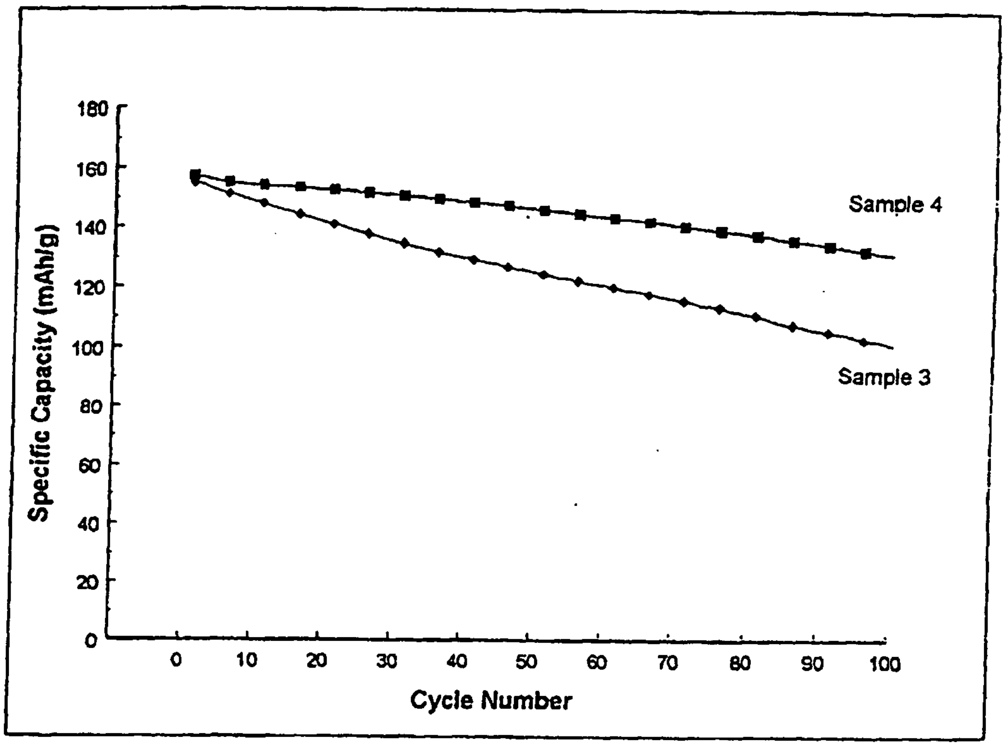

180
160
140
120
100
80
60
40
20
0
Specific Capacity (mAh/g)
0
10
20
30
40
50
60
70
80
90
100
Cycle Number
Sample 4
Sample 3

Fig. 7